BIOMATERIALS

CERAMICS MADE FROM CALCIUM HYDROXYAPATITE SYNTHESIZED FROM CALCIUM ACETATE AND POTASSIUM HYDROPHOSPHATE

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The properties of hydroxyapatite powder synthesized from calcium acetate and potassium hydrophosphate and hydroxide were investigated. The associated reaction product (ARP), whose basic component is potassium acetate, modifies the surface of the hydroxyapatite nanocrystals. The components of the ARP can play the role of a salt matrix by preventing coalescence of nanocrystallites and can also serve as a source for a sintering additive which is uniformly distributed due to adsorption during synthesis. A ceramic based on hydroxyapatite with a uniform microstructure and a maximum grain size of 300 nm was obtained by incorporation of sintering additives in the form of ARP at a temperature of 700°C. The ARP is the cause of different solid-phase processes and processes involving the liquid phase. The sites where these processes occur are the boundaries of the grains, which also restrains their growth.

Fabrication of ceramics based on hydroxyapatite (HAP) is one of the intensively evolving directions in medical materials science. Powders with high sintering activity must be used to fabricate high-quality ceramic materials. Such powders are usually synthesized by an existing chemical method. Precipitation of the powder from aqueous solutions of the corresponding components is the most common and simplest method of fabricating HAP. There are different methods of fabricating HAP in which phosphoric acid or soluble ammonium, potassium, and sodium phosphates and soluble potassium salts: nitrate, chloride, acetate, are used as the initial compounds (USSR Inventor's Certificate Nos. 710928 and 1450852; RF Patent Nos. 2038293 and 2050317).

The powders obtained contain a significant amount of associated reaction products (ARP) which are adsorbed on the surface of the powder during synthesis [1, 2]. After drying, the ARP can play the role of a rigid matrix that prevents aggregation of HAP particles less than 100 nm in size. During molding, the ARP present in the powder whose basic component is a soluble salt, for example, NH_4NO_3 or NaCl [1, 2], can play the role of a plasticizer. In heat treatment, the NH_4NO_3 salt will most probably not affect the occurrence of such a physicochemical process as sintering, since it decomposes before sintering begins. The compound NaCl has a relatively low melting point and due to the high volatility, can

go out of the intermediate product during heat treatment above this temperature. In examining the reaction of synthesis of HAP from calcium acetate and potassium hydrophosphate and hydroxide, we can predict that potassium acetate will be one of the basic components of the associated product:

$$10Ca(CH_3COO)_2 + 6K_2HPO_4 + 8KOH \rightarrow$$
$$Ca_{10}(PO_4)_6(OH)_2 + 20KCH_3COO + 6H_2O. \quad (1)$$
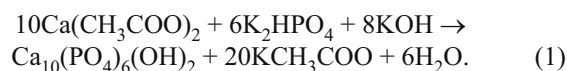
We also know that the acetate ion, which actively participates in ionic equilibria, decreases the concentration of free calcium ions in the solution due to formation of a $CaCH_3COO^+$ ion pair. Additional effects are introduced by hydrolysis of the acetate ion, and the buffer system formed stabilizes the pH of the reaction mixture. Another aspect of the effect is due to adsorption of the acetate ion on the surface of the HAP, which is much stronger than for the nitrate anion, for example [3]. Adsorption of acetate ions on the surface of the HAP crystallites formed will prevent them from growing, as predicted.

Different salts, including potassium KCl and calcium $CaCl_2$ chlorides, sodium Na_2CO_3 and potassium K_2CO_3 carbonates, and some others [4 – 6], have been used as sintering additives, but potassium acetate has not been examined in this role.

We investigated the properties of HAP powder synthesized from solutions of calcium acetate and potassium hydro-

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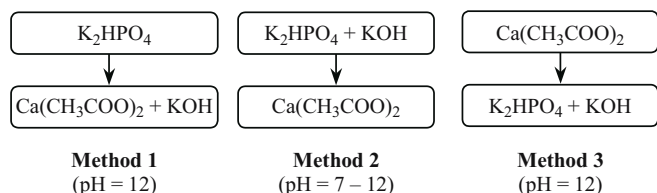[1] M. V. Lomonosov Moscow State University, Moscow, Russia.

Fig. 1. Scheme of synthesis of HAP powders.

Fig. 2. XPA of the synthesized powders obtained with methods 1, 2, and 3.

phosphate and hydroxide and elucidated the role of ARP in formation of the microstructure of ceramic materials.

HAP powders containing ARP whose basic component is potassium acetate were investigated.

The powders were synthesized according to reaction (1), by conducting it with three different schemes (Fig. 1) and changing the sequence of mixing the solutions of the initial substances. KOH was used in a 1.2-fold excess to provide for the necessary pH of the reaction during the entire synthesis process.

According to method 1, KOH was initially added to 1 liter of 0.5 M aqueous solution of calcium acetate. In the reaction of these components, a suspension of $Ca(OH)_2$ in an aqueous solution of potassium and calcium acetates was formed:

$$Ca(CH_3COO)_2 + 2KOH \rightarrow Ca(OH)_2\downarrow + 2KCH_3COO. \quad (2)$$
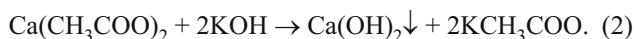
Only half of the calcium acetate was consumed for obtaining calcium hydroxide. Then 1 liter of a 0.3 M aqueous solution of calcium hydrophosphate was added to the suspension obtained by drops.

In this case, synthesis of HAP takes place both according to reaction (1) and according to the following reaction:

$$10Ca(OH)_2 + 6K_2HPO_4 \rightarrow$$
$$Ca_{10}(PO_4)_6(OH)_2 + 12KOH + 6H_2O. \quad (3)$$

According to methods 2 and 3, the reaction was conducted using a 0.5 M aqueous solution of calcium acetate and a 0.3 M aqueous solution of potassium hydrophosphate containing potassium hydroxide. In these cases, HAP is the only insoluble compound. In method 2, a mixture of the solutions of potassium hydrophosphate and hydroxide were poured into the calcium acetate and in method 3, calcium acetate was poured into the mixture of solutions of potassium hydrophosphate and potassium hydroxide.

TABLE 1

Method	Characterization of reaction	pH in reaction zone	Bulk density of powder, g/cm^3	Molding density, g/cm^3
1	Heterogeneous	12	0.51	1.49
2	Homogeneous	7 – 8	0.48	1.26
3	″	12	0.44	1.18
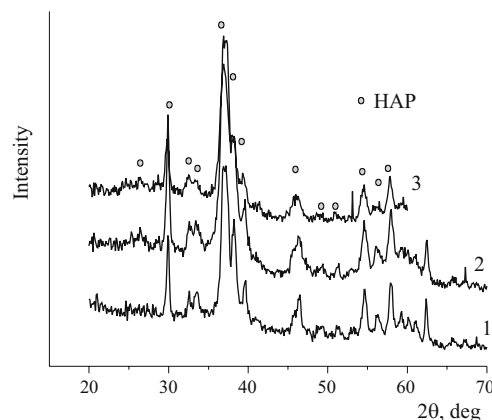
After mixing the solutions, the HAP suspension obtained was held in the mother liquor for 30 min. The sediment was filtered on a paper filter in a water-jet vacuum pump. The filtered sediment was dried in a thin layer at 20°C. The product obtained was degassed in a ball mill in acetone. The acetone : powder : ball ratio was equal to 1 : 1 : 3. After degassing, the powder was dried at 20°C for 2 h and passed through a sieve with 200 μm mesh size. The samples were molded into $3 \times 5 \times 10$ mm bars weighing approximately 0.2 g at a molding pressure of 100 MPa. The isothermal holding method was used to study the evolution of the structure. The samples were heated to different temperatures in the 600 – 1200°C range at the rate of 5 K/min and held at the final temperature for 6 h.

According to the XPA data, HAP were synthesized with these methods of combining the reagents (Fig. 2). A comparison of the weight of the powder obtained after drying with the weight calculated with reaction (4) indicated the presence of approximately 10 – 15%[2] ARP in it. After synthesis, the mother liquor contained potassium hydroxide and carbonate together with potassium acetate. Due to the important specific surface area, the synthesized hydroxyapatite adsorbs the ions contained in the solution: K^+, CH_3COO^-, CO_3^{2-}, and OH^-. However, no other compounds except for ARP were determined by XPA.

Potassium hydroxide is present because this reagent was used in excess to maintain the pH at the required level. Aqueous solutions of the alkali easily absorb atmospheric carbon dioxide, forming carbonates. Synthesis was conducted at a temperature of 60°C, which caused separation of a small amount of acetic acid, which is not an obvious product of reactions (1) and (2), from the reaction. The acetic acid content also decreased in the drying stage. These processes resulted in a decrease in the amount of potassium acetate in the ARP due to hydrolysis:

$$KCH_3COO + H_2O \rightarrow CH_3COOH\uparrow + KOH. \quad (4)$$

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[2] Here and below: mass content.

We can hypothesize that the amounts of the components of ARP, which consist of potassium acetate and potassium hydroxide and carbonate, are commensurate and consequently close to the sensitivity limit of XPA.

We should note that when carbonate ions are present in the solution, the proper conditions are created and it is probable that carbonate hydroxyapatite (CHAP) will be formed. The presence of carbonate ions in the synthesized powder was confirmed by the IR spectroscopic data. In addition, substitution of Ca^{2+} ions by K^+ in synthesis of HAP, which requires charge compensation and also causes entry of carbonate ions in the structure and formation of K-substituted CHAP, is also possible.

The synthesized powder is noncrystalline HAP powder with an individual crystallite size of $30 - 50$ nm after separation of sediment and degassing. According to the data from granulometric analysis (FRITSCH, Analisette, Germany), the average aggregate size for all synthesized powders is in the $3.0 - 3.5$ μm range. Like most chemically synthesized powders, the ARP obtained has at the minimum a two-level structure and consists of aggregates that contain nanocrystallites. Due to the presence of a small amount of ARP, the individual particle (primary aggregate) can be considered as a nanocomposite in which ARP acts as the matrix and nanocrystallites of ARP are distributed in this matrix.

Table 1 reports some rheological properties of the synthesized powder. The bulk density is $0.44 - 0.51$ g/cm^3 and the molding density is $1.18 - 1.49$ g/cm^3. The ARP in the powder can play the role of a temperature process binder, decreasing the friction between the particles and causing their reciprocal movement in molding. These properties of ARP allowed molding without use of additional temporary binder. The higher molding density of powder obtained with the heterogeneous reaction in comparison to the powders synthesized by homogeneous reactions can be attributed to the higher RAP content (Fig. 3).

Weight losses of the powders of up to 25% in heating to 1150°C were found in thermogravimetric analysis (see Fig. 3, Perkin Elmer thermoanalyzer, heating rate of 10 K/min). The weight losses took place in several stags during heating.

In the first stage, $1 - 6\%$, up to the temperature of 150°C, the weight losses can be correlated with elimination of adsorbed water and acetone, since disaggregation of the powders was conducted in acetone.

The second stage reflects decomposition of potassium acetate into potassium carbonate and acetone $(3.5 - 5.0\%)$ according to the reaction:

$$2CH_3COOK \rightarrow K_2CO_3 + (CH_3)_2CO\uparrow. \qquad (5)$$
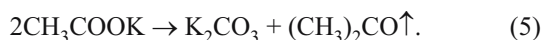
This process takes place in the $300 - 400°C$ temperature range, which is in agreement with the published data for potassium acetate.

The third stage $(3 - 5\%, 700 - 800°C)$ is most probably correlated with decomposition of potassium carbonate, CHAP, K-substituted CHAP, and the possible occurrence of
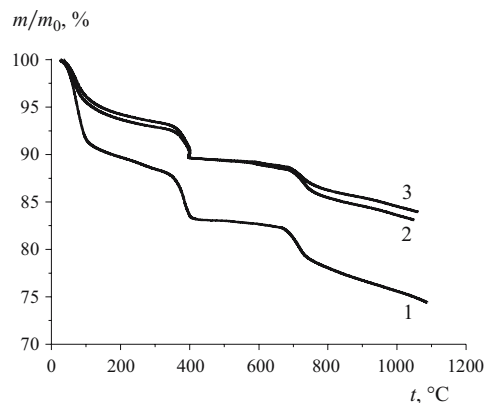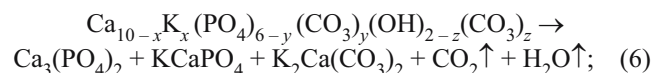

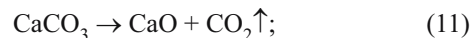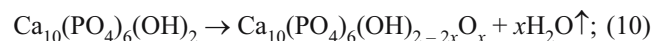**Fig. 3.** Measurement of weight in continuous heating of powders obtained with methods 1, 2, and 3.

reaction of phosphates with the potassium carbonate or double calcium potassium carbonate with formation of double potassium calcium phosphate:

$$Ca_{10-x}K_x(PO_4)_{6-y}(CO_3)_y(OH)_{2-z}(CO_3)_z \rightarrow$$
$$Ca_3(PO_4)_2 + KCaPO_4 + K_2Ca(CO_3)_2 + CO_2\uparrow + H_2O\uparrow; \quad (6)$$

$$Ca_3(PO_4)_2 + K_2Ca(CO_3)_2 \rightarrow KCaPO_4 + CaCO_3 + CO_2\uparrow; \quad (7)$$

$$Ca_3(PO_4)_2 + K_2CO_3 \rightarrow KCaPO_4 + CO_2\uparrow. \qquad (8)$$

Reaction of tricalcium phosphate and calcium carbonate in the presence of water vapors with formation of hydroxyapatite is also possible:

$$Ca_3(PO_4)_2 + CaCO_3 + H_2O \rightarrow Ca_{10}(PO_4)_6(OH)_2 + CO_2\uparrow. \quad (9)$$
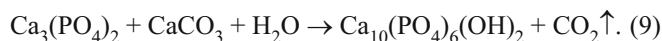
The further weight losses, $3.5 - 6.0\%$, during heating at temperatures above 800°C could be due to partial dehydration of HAP with formation of oxyhydroxyapatite, with possible decomposition of calcium carbonate, and double calcium potassium carbonate:

$$Ca_{10}(PO_4)_6(OH)_2 \rightarrow Ca_{10}(PO_4)_6(OH)_{2-2x}O_x + xH_2O\uparrow; \quad (10)$$

$$CaCO_3 \rightarrow CaO + CO_2\uparrow; \qquad (11)$$

$$K_2Ca(CO_3)_2 \rightarrow CaO + K_2CO_3 + CO_2\uparrow. \qquad (12)$$

An increase in weight loss was also observed with an increase in the temperature in studying the samples by the isothermal holding method (Fig. 4). At 1200°C, the weight losses reached $29 - 30\%$. Greater weight losses at relatively low (under 400°C) temperatures were observed in the powder obtained with the heterogeneous reaction (method 1). In this temperature region, water and acetone are liberated, and the amounts can be larger than in the powders obtained with the homogeneous reactions (methods 2 and 3). The powders obtained with the heterogeneous reaction probably have a higher specific surface area caused by the smaller particle
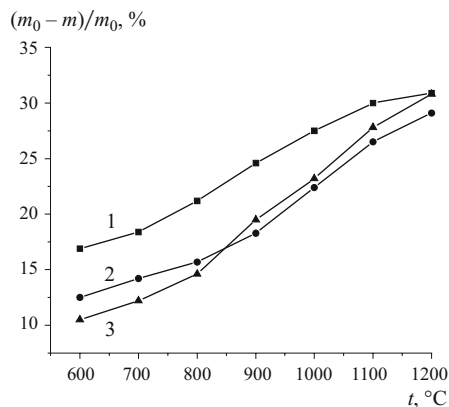
$(m_0 - m)/m_0$, %

Fig. 4. Weight loss as a function of the temperature of powder samples obtained with methods 1, 2, and 3.

L/L_0, %

Fig. 5. Dilatometric curves of powder samples obtained with methods 1, 2, and 3.

$(L_0 - L)/L_0$, %

Density, g/cm^3
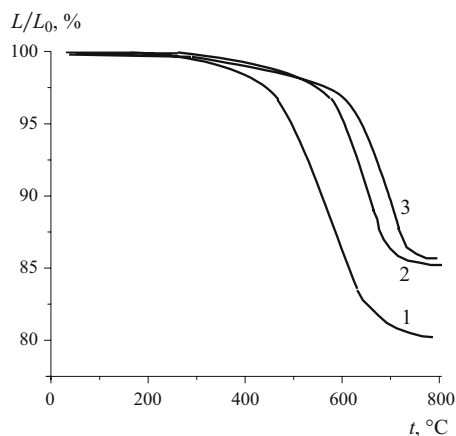

Fig. 6. Temperature dependence of linear shrinkage (*a*) and density (*b*) of samples of powders made with methods 1, 2, and 3.

size and they can consequently adsorb a larger amount of RAP.

The dilatometric curves of these samples (LIR-1400 dilatometer, Russia; heating rate of 7 K/min to 1000°C) are shown in Fig. 5. In sample 1, shrinkage began at 200°C, versus at 280°C for samples 2 and 3. The maximum shrinkage rate of sample 1 fell within the 460 – 640°C temperature range, and in the 590 – 720°C range for samples 2 and 3. The shrinkage slowed on further heating. According to the data from the dilatometric analysis, the shrinkage reached 20% at 800°C in sample 1 and 15% in samples 2 and 3. The cause of such low values for the initial linear shrinkage temperatures and the temperature range of the maximum shrinkage rate could be the formation of an eutectic melt with a low melting point in the system formed by components of RAP whose melting point is 292°C for potassium acetate, 405°C for KOH, and 894°C for K_2CO_3.

The dependences of the linear shrinkage and density on the temperature determined by isothermal holds are shown in Fig. 6. The curves for all compositions have a similar charac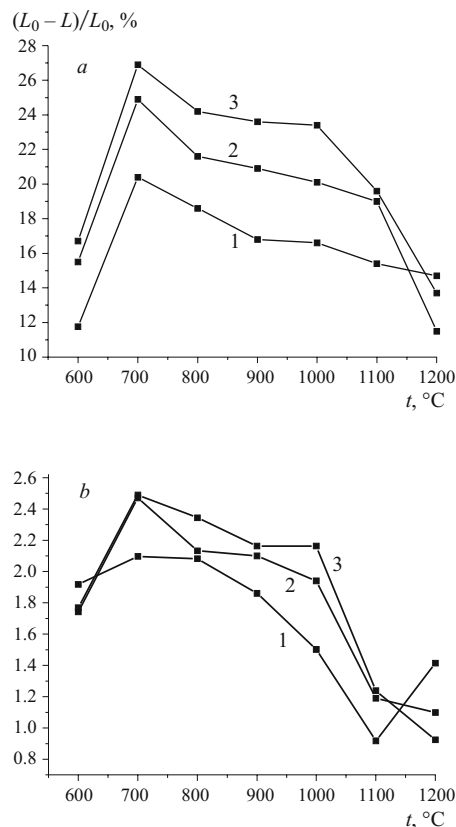ter. In heating to 700°C, the density and shrinkage of the samples increased. The samples fired at 700 – 800°C were semitransparent. Firing the samples at higher temperatures (800 – 1200°C) reduced the linear shrinkage. The decrease in the shrinkage and density could have been due to decomposition of the carbonates present in the samples. Based on the external appearance of the samples, we hypothesized that gas formation takes place intensively in the presence of the melt. The shrinkage over the height was less than the shrinkage over the length, manifested in the shape of the curves of the density as a function of the temperature. An increase in the density which could have been due to a decrease in the viscosity of the melt present in the sample and collapse of previously arising cavities, was observed for sample 1 at 1200°C.

The grain size in the ceramic fired at 700°C did not exceed 300 nm (Fig. 7*a*). Formation of a homogeneous microstructure with a small grain size was possible due to the low firing temperature and the presence of melt with a low melting point. The amount of this melt is small. According to the data from thermal analysis, the amount of potassium carbonate did not exceed 4%. However, the precise amount and composition of the melt were not determined, and it could only hypothetically belong to $K_2O – CaO – P_2O_5$ or $CaO – P_2O_5 – K_2CO_3$ systems if the components of ARP react with the basic crystalline phase represented by CHAP. According to the XPA data, $K_2Ca(CO_3)$ and $KCaPO_4$ were detected in the ceramic fired at 700°C for 6 h, together with
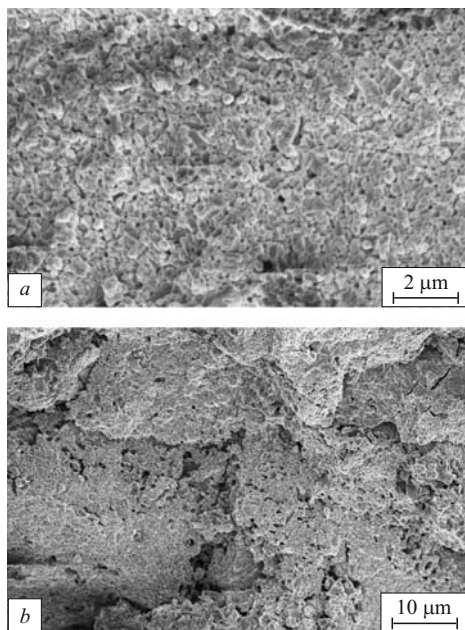
Fig. 7. Microstructure of a ceramic made from powders according to method 2 after firing at 700°C (*a*) and 1100°C (*b*) for 6 h.

the HAP phase. These phases, as hypothesized previously in analyzing the thermal analysis data, could be the result of complex solid-phase reactions or could have crystallized from the melt on cooling.

The grain size in the ceramic fired at 1100°C did not exceed 1 μ and was 500 nm on average (Fig. 7*b*). The photomicrograph of a chip of the ceramic shows the loose structure of the material, and the grains in the ceramic are of approximately the same size. According to the XPA data, $KCaPO_4$ and CaO were detected together with the ARP phase in the ceramic fired at 1100°C for 6 h. This method of forming the pore structure in the HAP or CHAP material could be used if CaO were not formed, as its presence is undesirable in materials for bone implants.

The methods of synthesizing HAP from solutions are simple and convenient and allow obtaining highly disperse powders with a maximum size of the individual crystallites of 100 nm. Such powders have high sintering activity and can be used for production of nanoceramics. By varying the initial components (soluble calcium phosphates and salts), sintering additives or additives that modify the surface of the nanopowder particles can be incorporated as ARP. The adsorbed ARP is uniformly distributed over the boundaries of the nanocrystallites, decreasing the surface energy and preventing the individual nanocrystallites from sticking together. For this reason, nanoceramics can be obtained by ordinary sintering, without the use of colloidal formation or hot molding.

REFERENCES

1. T. V. Safronova, M. A. Shekhirev, V. I. Putlyaev, and Yu. D. Tret'yakov, "Ceramic materials made of hydroxyapatite synthesized from solutions of different concentration," *Neorg. Mater.*, No. 8, 1 – 10 (2007).
2. T. V. Safronova, M. Yu. Steklov, V. I. Putlyaev, and M. A. Shekhirev, "Na-substituted Ca-deficient carbonate hydroxyapatite for production of ceramic materials," *Konstruk. Kompozit. Mater.*, No. 4, 39 – 43 (2006).
3. A. A. Stepuk, A. G. Versov, V. I. Putlyaev, and Yu. D. Tret'yakov, "The influence of , CH_3COO^-, and Cl^- ions on the morphology of calcium hydroxyapatite crystals, *Dokl. Akad. Nauk*, **412**(2), 211 – 215 (2007).
4. V. Yu. Bibikov, V. V. Smirnov, I. V. Fadeeva, et al., "Enhancement of sintering of carbonate hydroxyapatite ceramic for bone implants," *Perspektiv. Mater.*, No. 6, 43 – 47 (2005).
5. W. Suchanek, M. Yashima, M. Kakihana, and M. Yashimura, "Hydroxyapatite ceramics with selected sintering additives," *Biomaterials*, **10**, 923 – 933 (1997).
6. T. V. Safronova, Yu. D. Tret'yakov, V. I. Putlyaev, et al., "Nanoceramic based on calcium hydroxyapatite," *Konstruk. Kompozit. Mater.*, No. 1, 22 – 31 (2007).